(54) CELLULATED GLASSY BODIES AND THEIR METHOD OF MANUFACTURE

(71)   We, CORNING GLASS WORKS, a corporation organised under the laws of the State of New York, United States of America, of Corning, New York, United
5 States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the fol-
10 lowing statement:

This invention relates to cellulated glassy bodies.

Foamed or cellulated glass bodies, that is, inorganic heat-resistant bodies expanded by
15 the internal development of non-connecting gas-filled cells while the material is in a coalesced or fused state, are well known. Similarly foamed glass products, having densities of the order of 0.15 to 0.30 grams/
20 cc, have been in use for several years to provide buoyancy, light weight and thermal installation in conjunction with resistance to heat and moisture penetration.

Such commercial products are customarily
25 produced from premelted glass. In general, the process involves premelting a suitable glass composition, pulverising the admixture with chemically reactable gas-producing agents such as a carbon reducing agent in
30 conjunction with an oxidising agent, depositing a layer of the pulverised mixture in a closed pan, heating to a foaming temperature of about 800 to 900°C (1470 to 1650°F) and then annealing over a period of several
35 hours. The products and processes of production are technically satisfactory, but high production costs have imposed a limit on areas of utility for these foamed glass products. Major economic factors are glass
40 batch cost, mould equipment, and separate melting, grinding and foaming operations.

It has long been recognised that direct foaming of either a natural raw material or waste slag material into large bodies
45 should provide a distinct economic advant-

age. Accordingly, numerous methods of foaming molten slag materials have been proposed. However, these have not been commercially adopted except in the production of light weight aggregate, normally 50 small pellets, for concrete mixtures. There appears to be a basic difficulty in obtaining uniform and adequate cellulation of slag material as it is obtained in the molten state. 55

It has been proposed to directly foam either an unmelted glass batch or natural minerals since direct foaming would avoid the premelting step. In spite of the readily apparent economic advantage, these pro- 60 posals have not been commercially adopted to make large bodies. It has proven difficult to uniformly cellulate an unmelted glass batch due to the occurrence of batch reactions and segregation during the foaming 65 process. The use of natural minerals can obviate these problems but requires cellulating temperatures on the order of 200 to 500°C. (300 to 900°F) higher. At such temperatures, the carbon reducing agents here- 70 tofore conventionally employed to foam premelted glass cannot provide adequate cellulation. The use of clays or shales as batch ingredients have been proposed but also normally require high cellulation tem- 75 peratures.

Due to the requirement of a reducing atmosphere, it is necessary in most cases to contain the batch in a mould during cellulation. The mould can be a metal mould 80 for lower temperature glass systems but in the case of the higher cellulation temperatures of clays or shales the batch is fed into ceramic moulds. The batch is then heated to the cellulation temperature and 85 held thereat while the body expands. This type of operation presents several problems which arise from the fact that a ceramic mould is normally required. These problems include feeding the match into a mould. 90

removal of the cellulated body from the mould, cleaning the mould, the fairly large capital investment in the moulds, their large mass and heat capacity and their fragility. Thus, it has been shown to be highly desirable to produce cellulated glassy bodies without utilising a restraining mould to hold the batch materials and at a temperature where thin firing platforms can be used.

We have invented a unique batch composition which may be cellulated, at temperatures normally below those normally used in such processes, without restraint; and wherein the shape of the cellulated body maintains the configuration of the preformed batch material.

The invention provides a batch for making a cellulated glass body comprising, in weight percent on the anhydrous basis, at least 50% by weight of at least one rock which is volcanic ash, weathered volcanic ash, and/or clay, at least one alkali metal containing material in which sodium hydroxide and/or sodium silicate constitutes at least 25% by weight of the total content of such alkali metal containing material, and a cellulating agent which is carbon and/or a compound which thermally decomposes below the cellulating temperature and has carbon as decomposition product, the total rock, alkali metal containing material, and cellulating agent being at least 75% by weight of the anhydrous batch and the batch comprising, in weight percent as calculated from the batch on the oxide basis, 10% to 20% total alkali metal oxide, SiO_2 and Al_2O_3 in the ratio of from 3:1 to 6:1, and a total content of alkali metal oxide, SiO_2 and Al_2O_3 that is at least 93%.

The alkali metal containing material is added as a 'flux', that is a material which reacts with other batch materials at a temperature below that at which such other batch materials normally melt, thus lowering the batch melting temperature. Hence any reference to a flux refers to the alkali metal containing material. A rock, as used herein, as defined as a naturally occurring aggregate of minerals. Clays are preferred and the discussion hereinafter will refer specifically thereto, although the other rocks, volcanic ash and the weathered volcanic ash, can be functional equivalents of clay. The aforementioned batch ingredients are mixed and, when heated to temperatures as low as 800°C, will cellulate to form a light weight glassy body having a fine uniform cell structure. The batch may be pressed or otherwise shaped into a desired configuration and then fired on thin flat plates. During the cellulation, the body expands but maintains the same configuration as the preformed batch material.

The anhydrous batch contains at least 50% by weight of rock, preferably clay,

with additions of flux and cellulating agents. We have found that at least 25% of the total flux must be added to the batch as sodium hydroxide (NaOH) and/or sodium silicate (Na_2SiO_3). Moreover, at least 80% by weight of the total flux is preferably Na_2O. The sodium hydroxide appears to react with the clay, to produce a chemical comminution thereof, so as to yield more uniform cellulation and sodium silicate or sodium alumino-silicate *in situ*. The alkali silicate, added or formed *in situ*, provides a more rapid fluxing action. The cellulating agent is an organic material which will thermally decompose and yield carbon as one of the decomposition products. One of the preferred cellulating agents is sodium acetate. The silica/alumina (SiO_2/Al_2O_3) ratio, as calculated from the batch on the oxide basis, must fall within the ratio of 3:1 to 6:1 with the total flux being between 10% and 20%. Furthermore, impurities such as CaO, MgO, BaO and Fe_2O_3 should not exceed 7% as calculated from the batch on the oxide basis. The aforementioned ratio is essential so as to provide a glassy matrix which will be within the proper viscosity range at low firing temperature so as to entrap the cellulating gas.

The batch ingredients are finely ground and mixed so as to provide an intimate homogeneous admixture. The mixed batch is then pressed or otherwise shaped to the desired configuration. The shaped body is then fired on relatively thin supporting plates which allow the body to be heated and expand uniformly. The body and supporting plate are then subjected to a cellulation firing and annealing schedule. This cellulation firing comprises a rapid heating to a temperature at which cellulation will occur but at which the supporting plates will not distort or otherwise deteriorate. The body is held at the cellulation temperature for a length of time sufficient to achieve the minimum density attainable at that temperature without incurring bubble coalescence. Thereafter, the body is rapidly cooled to the annealing temperature and then slowly cooled to room temperature through an annealing schedule. The shape of the body will determine whether or not it is to be fired on supporting plates. For example, the batch may be formed into pellets and the pellets may be free foamed in place but not necessarily on supporting plates. The foamed glassy pellet may be used as light weight aggregate for additions to concrete or other materials wherein it is desirable to reduce the bulk density of the material. The batch may also be pressed into a green billet having a tile-like shape and then foamed, without restraint, to form a tile of the same configuration as the green billet.

The raw batch material comprises rock, preferably clay, additive alkali metal oxide fluxes including NaOH and/or Na_2SiO_3 and a cellulating agent. The combination of clay,
5 additive alkali metal oxide fluxes and the cellulating agents comprise at least 75% by weight of the anhydrous batch with up to 25% of the batch being added silica, alumina ond/or grog. The term 'grog' is
10 defined as being waste fired batch material that has been finely ground. If the silica exceeds the amount disclosed therein, the batch is too viscous to allow proper foaming. If the batch is too high in alumina, the
15 liquidus of the batch is too high to allow appropriate foaming; and if the alkali metal oxide exceeds that disclosed, the batch is too fluid to allow proper foaming. Conversely, if the silica is below the minimum, the batch
20 is not sufficienly viscous; if the alumina is below the minimum, the batch may be too fluid; and, if the alkali metal oxide is below the minimum, the batch may be too viscous for proper cellulation.
25 The batch ingredients are determined on two bases: the first is the oxide basis as calculated from the batch and the second is the anhydrous basis which represents the raw batch ingredients without added water.
30 However, the clay may contain up to 15% adsorbed water in addition to any water of hydration. Adsorbed water is that water which can be removed from the clay by heating at a temperature between 110°C
35 and 150°C. The water of hydration can be removed by heating at 500 to 700°C.

One class of naturally occurring materials which contain two of the main components, silica and alumina, are clays. Clays are
40 plastic, earthy, fine-grained materials, predominantly composed of clay minerals. Clay minerals are generally platy, hydrous aluminium silicates that can have appreciable quantities of iron, alkalies and alkaline

earths. We have found that clays contain- 45 ing substantial quantities of illite and/or smectite minerals are particularly desirable for foaming. However, we prefer to use clays containing the following members of the smectite group: montmorillonite, bei- 50 dellite, and nontronite. In particular, clays containing montmorillonite are preferred. The minerals of the smectite group are preferred since they have a high silica to alumina ratio and can absorb into their 55 structure certain organics which can act as cellulating agents. The theoretical formula for smectite minerals is $(OH)_4$ $Si_8Al_4O_{20}.H_2O$ while the theoretical composition, in weight per cent, is 66.7% SiO_2, 60 28.3% Al_2O_3 and 5% H_2O. Various lattice substitutions occur which characterise the different members of the smectite group. In montmorillonite, magnesium and sodium partially replace aluminium; in beidellite, 65 aluminium and sodium partially replace silicon; and in nontronite, aluminium and sodium partially replace silicon while iron replaces aluminium.

In addition to the clay minerals, the clays 70 also contain other minerals. We have determined that the silica to alumina ratio of the batch should be between about 3:1 and 6:1. Thus, it is desirable to use clays containing clay minerals that have as high a 75 silica to alumina ratio as possible. For example, in a bentonite clay, having as its predominant clay mineral montmorillonite, we have found a silica to alumina ratio of 5:1. However, the montmorillonite has a 80 ratio of 4:1. Thus, the remainig silica is obtained from other non-clay minerals such as cristobalite. Listed below in Table I are several clays which can be used, their major clay minerals, the silica to alumina ratio 85 and the clay composition, which is on a weight percent basis.

Table I

Clay	Principal Clay Mineral	SiO_2/Al_2O_3	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Balance
Wyoming Bentonite	montmorillonite	2.8	66.0	23.5	0.7	2.4	3.9	1.4	0.1	2.0
Horseheads, N.Y. Clay	illite	3.5	66.0	19.2	7.5	0.5	2.0	0.6	1.5	2.7
Gonzales Bentonite	montmorillonite	4.8	77.0	16.0	1.4	1.3	3.0	0.8		—
Japanese Bentonite	montmorillonite	5.6	79.0	14.0	1.9	1.7	2.6	0.6	0.5	—

To those batches wherein the clay does not provide the desired silica to alumina ratio, finely-ground silica and/or alumina may be added in sufficient amounts to achieve the desired ratio.

It is known that in foaming reactions the finer the particle size or grain size of the reactants, the more uniform is the resulting foam structure. From this point of view, bentonite clays containing substantial amounts of montmorillonite are high desirable; since the grain size of the clay is normally less than 5 microns. If other clays are selected with the proper grain size but not the proper silica to alumina ratio, the additive silica and/or alumina should have a sufficiently small particle size to allow proper mixing. This would normally require a particle size of less than five microns. Similarly, if the other rocks are substituted for clay, they must have a particle size less than 5 microns. In any case, the grain size of the clays or particle size of the rock, silica or alumina should be less than 5 microns.

In a preferred embodiment, bentonite clays having montmorillonite as the principal clay mineral are the most desirable since they normally have the proper silica to alumina ratio and are extremely fine grained. Bentonite clays are readily available throughout the world with a principal deposits in the Wyoming-South Dakota area of the United States. Moreover, in a particular embodiment, we prefer that the clay, preferably bentonite, comprise between 70% and 87% of the anhydrous batch.

Bentonite clays are the result of the weathering of volcanic ash. A most important distinction between volcanic ash and bentonite is the grain size. The grain size of volcanic ash can be in excess of 5 microns. However, from a compositional point of view, bentonite clay and its precursors are essentially the same. Therefore, volcanic ash and the weathered intermediates between volcanic ash and bentonite are functional equivalents of bentonite clays provided that their grain size is less than about 5 microns.

In order to achieve the proper viscosity for foaming, it is necessary to add a flux to the clay. In other foaming systems, for example, MgO, CaO, and Fe_2O_3 are considered as fluxing agents; but at the low temperatures used in this process, only the alkali metal oxides (R_2O) are effective fluxes. More specifically, we have found that soda (Na_2O) containing compounds are the best fluxes for clays, in the 800 to 950°C temperature range. We have found that the total amount of flux should be between 10% and 20% by weight on the oxide basis as calculated from the batch. In these systems, at least 80% of the total flux should preferably be Na_2O, with Li_2O and K_2O normally making up the remaining flux. Moreover, at least 25% of the total flux must be Na_2O which has been added as NaOH and/or Na_2SiO_3.

We have found that the sodium hydroxide

reacts with the clay so as to reduce the grain size still further, thereby assuring even better cellulation and more uniform reaction. It is believed that the sodium hydroxide reacts with the clay mineral, particularly montmorillonite, to form an amorphous sodium-aluminosilicate. The fusion caused by the alkai silicate reduces the minimum cellulating temperature for the entire batch. In addition, the reaction between the sodium hydroxide and clay at room temperature produces a cementitious reaction product, that is at least partly sodium silicate, which tends to strengthen the green body. Rather than using the sodium hydroxide which will form sodium silicate, a sodium silicate solution may be introduced into the batch. When only 25% by weight of the Na_2O is added as NaOH and/or Na_2SiO_3, the balance of the added flux may be in the form of another sodium salt such as sodium carbonate. We have found that either NaOH or Na_2SiO_3 is necessary in order to produce an acceptable foam. Other alkali-containing compounds may be substituted for the sodium salt but not for the NaOH or Na_2SiO_3. However, if, for example, lithium and/or potassium salts are used, the total of the oxide thereof should not exceed about 20% of the total flux. Typically, the added fluxes may be compounded as follows: at least 25% by weight of the total flux being Na_2O added as NaOH and/or Na_2SiO_3 with the remaining added flux being added as Na_2CO_3 and up to 20% flux being added as Li_2CO_3, K_2CO_3, LiOH or KOH.

We prefer to use batches wherein the added flux containing materials are equal parts by weight NaOH and Na_2CO_3. In a particular embodiment, we prefer that the total NaOH and Na_2CO_3 comprise between 12% and 18% of the anhydrous batch.

We have found that, since the temperatures at which the batch fuses to the proper viscosity are relatively low, organic cellulating agents can be used rather than the inorganic cellulating agents of the prior art. Other cellulating gases may be available from the clay. As the batch is heated, the clay loses its adsorbed water and then its water of hydration; if the batch has fused so as to form a viscous glass before dehydration is complete, the water of hydration may form steam and contribute to the expansion of the glass. Thus, there can be two cellulating agents. One is the water of hydration available in the clay, and the second is gases produced due to the organic cellulating agent. We have found that the preferred organic cellulating agents are those compounds which will thermally decompose, at a temperature below the desired cellulating temperature, leaving as one of the decomposition products carbon which

may react to form CO or CO_2. The CO or or CO_2 will then act as a cellulating gas. Carbon in the form of carbon black or graphite may be used. However, we prefer to use an organic compound or metal salt of an organic compound having carbon as a decomposition product. The weight of organic compound required is related to theamount of free carbon produced in the decomposition. For example, carbohydrates and compounds containing like amounts of oxygen can form CO and H_2 on heating but little, if any, carbon is formed. Thus, sodium oxalate will not work as a foaming agent since no carbon is produced. (see equation 1.)

(1) $Na_2C_2O_4 \longrightarrow Na_2CO_3 + CO$
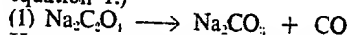
However, sodium acetate works quite well. (See equation 2.)

(2) $2NaC_2H_3O_2 \longrightarrow Na_2CO_3 + CO + 2C + 3H_2$
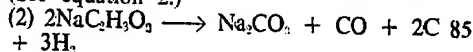
Thus, it is seen that one-half the carbon in sodium acetate is theoretically available for cellulation. In order to achieve the desired densities, the carbon available for cellulation should be between 0.1 and 1.0% by weight of the anhydrous batch. Therefore, in using an organic foaming agent, the amount required is calculated from the amount of carbon formed during the thermal decomposition. For example, to have 0.15% free carbon in a batch would require the addition of 1.0% sodium acetate. We have found sodium acetate to be particularly effective in amounts between 0.75% and 1.25% of the anhydrous batch. Table II below lists several operative and inoperative organic compounds.

Table II

Inoperative	*Operative*
1. Lignosulphonates	1. Sodium lauryl sulphate
2. Sugar	2. Sodium oleate
3. Starch	3. Sodium stearate
4. Guanidine hydrochloride	4. Sodium succinate
5. Hydrocarbons that vaporise or sublime	5. Sodium salicylate
6. Sodium oxalate	6. Sodium propionate
7. Sodium tartrate	7. Calcium acetate
	8. Ferrous acetate

If there is an excess of the cellulating agent present, it is difficult to control the reaction, while if there is an insufficient amount present, the desired density cannot be obtained. In general, it seems that the cellulating agent is effective in producing a minimum density under a given set of conditions, but only up to a maximum concentration of that cellulating agent; above the maximum concentration thereof, there appears to be no benefit in further increase in the concentration of the foaming agent.

A batch consisting of 100% of the afore-mentioned raw batch ingredients may be used and foamed to provide the desired product. However, it may be desirable to add to the batch a small amount of grog. Grog is fired batch material which has been reground to a granular form. The addition of this grog aids in producing a crack-free body. The amount of grog which may be introduced is related to the density which is desired. For a given set of conditions, larger additions of grog will generally increase the resultant density. In our process, wherein it is desired to produce products of density on the order of 0.4 grams/cc, additions of more than 25% by weight grog are undesirable.

The clay, flux and cellulating agent are mixed and ground together in a ballmill so as to obtain a fine, intimately mixed particulate batch. The materials are ground for whatever length of time is necessary to assure proper sizing and mixing. We have found that ballmilling is the best technique for obtaining the desired intimate, homogeneous and uniform batch. Normally, the finer the particle size the better; however, there are apparatus limitations which limit the minimum particle size which can be obtained. Most often the batch will be pressed, in a standard ceramic press, so as to form a tile or other similar body. If simple rectangular shapes are desired, the powder, as milled, can be pressed. However, in order to form a complicated shape by pressing, it is necessary to form the batch into granules. The mixed batch is first compacted by passing it through rollers and thereafter granulated so as to provide a more workable batch material. The size of the granules should be such that they will pass through a 14 mesh U.S. Standard Sieve screen but not through a 100 mesh screen. The granulated batch may then be moistened by a fine water spray. The weight of the added water can be up to 7% of the weight of the anhydrous batch; in other words, the weight of the anhydrous batch plus the added water can be up to 107% of the anhydrous batch. The water is added primarily to provide green strength for the body when it is formed. The granulated batch is then formed into the desired configuration. Moreover, with the further addition of still more water, up to a total of 15% by weight, the batch may be extruded, pelletised or shaped to configurations other than those available through pressing.

Since the batch is preformed to the desired configuration and expands in order to accommodate the expansion of the gas in the body, the body is fired without restraint. Normally, the larger tile-like bodies are supported during firing on a heat-resistant perforated metal sheet, which has been coated with a material which allows the body to expand without its sticking to the metal sheet. We have also found that thin glass-ceramic sheets of low thermal expansion, 0.060 inch thick, may be used. The sheet is normally very thin so that the heat transfer characteristics thereof are quite uniform. As the body is fired and the cellular structure forms, the body expands and is able to expand in all directions since it will not stick or adhere to the sheet. The preferred firing schedule is a rapid heating to the cellulating temperature and a hold thereat for a length of time sufficient to achieve the minimum density. After cellulation, the body is then cooled through an annealing schedule so as to avoid cracking and the build-up of internal stresses in the body. From a general point of view, we have found that the idealised schedule is applicable for most pressed bodies and pellets. With all other factors remaining constant, we have found that, in order to achieve the desired densities, a foaming temperature between 800 to 950°C (1560 to 1740°F) is necessary. The minimum temperature is related to the formation of the glass and entrapment of the gas. The maximum temperature is related to the distortion of the support plates. The length of time at firing temperatures between 800 and 950°C can vary between 2 and 15 minutes, depending upon section size and firing temperature. However, if it were not essential to use thin support plates and the uniformity of the cellular structure were not critical, then temperatures in excess of 950°C (1740°F) could be used for foaming. For example, pellets could be expanded on ceramic or heavy metal substrates at temperatures in excess of 950°C (1740°F). A typical firing schedule for a pressed body having a maximum cross-sectional thickness of approximately 3/4″ would be to heat the body to 900°C at a rate faster than 90°C/minute: hold at 900°C for 10 minutes; and then cool to room temperature in approximately 40 minutes. The fired body has a same configuration as the preformed unfired body, and has undergone a linear expansion of 45%. Other schedules can be developed for bodies of various sizes and configurtions.

The unique features of the fired product are that it is strong, light weight, inexpensive to produce, has an extremely uniform cell size and distribution thereof, has a closed cell structure and maintains the configuration of the pressed body. Normally, the cells are of a generally spherical shape with few, if any, cells being larger than approximately 1¼″ diameter. This is highly advantageous since, if the sphere size is increased or the sphericity decreasese, thin spots in the walls can be created, which

weaken the body as well as reducing the desired impermeability to moisture. Due to an almost total loss of foaming agent at the surface of the body, the surface thereof is somewhat denser than the interior portion. The density of the resultant product is normally less than 0.5 grams/cc, when the body is fired at temperatures less than 950°C. However, with changes in the firing schedule and changes in the batch composition, densities as low as 0.15 grams/cc or as high as 0.65 grams/cc can also be produced. The volume thermal coefficient of expansion of the resultant bodies is on the order of 80 to 90 × 10^{-7}/°C. Since the body is a foamed glassy body with residual undissolved compounds, a reproducible exact expansion is difficult to obtain and thus the coefficients of expansion are averages thereof. The glassy portion of the cellulated body is basically an alkali aluminosilicate having minor amounts of the alkaline earth metal oxides therein. The range of glass compositions is set forth in weight per cent on the oxide basis as calculated from the batch below:

(1) total SiO_2 between 50 and 80%,
(2) total Al_2O_3 between 10 and 25%,
(3) total R_2O between 10 and 20% with Na_2O between 8 and 20%,
(4) total impurities between 0 and 7%,
(5) SiO_2 and Al_2O_3 in the ratio of between 3:1 and 6:1.

The modulus of rupture (MOR) for bodies having a density of the order of 0.65 grams/cc is of the order of 550 psi; while, when the density is 0.15 grams/cc, the MOR is of the order of 150 psi. The gas content of the cells was analysed and determined to be primarily CO_2, CO, N_2 and H_2O. The glassy portion of the cellulated body is a partially melted glass containing minor amounts of non-glassy phases including alpha quartz, cristobalite and plagioclase feldspar.

Batches which are prepared within the limits set forth above, by the selection of various combinations of the clays, fluxes and cellulating agents as set forth herein, can be treated according to the methods and firing schedules set forth so as to produce acceptable cellulated bodies. Therefore, the following examples are set forth as illustrative of the product and process and not as specific limitations thereon.

Example 1

A batch to be foamed was prepared from the following batch ingredients:

(1) 83 pounds of an air floated Gonzales bentonite clay, having as its principal clay mineral montmorillonite, and an approximate oxide composition in weight per cent as follows: 77% SiO_2, 16.0% Al_2O_3, 0.8% Na_2O, 0.5% K_2O, 1.3% CaO, 3.0% MgO and 1.4% Fe_2O_3. This clay also contained about 10% adsorbed water and 6% water of hydration.
(2) 8 pounds anhydrous granular sodium hydroxide;
(3) 8 pounds anhydrous granular sodium carbonate; and
(4) 1 pound anhydrous powdered sodium acetate.

The above ingredients were mixed and then ballmilled for two hours to ensure adequate mixing. The mixed batch was then blended with 25 pounds of −14 mesh grog and 6 pounds of water was added, by spraying to cause some granulation.

The granulated batch was fed into a mould and pressed at 5000 psi to form a green body $\frac{1}{2}$″ × $\frac{1}{2}$″ × 4″. The bar was then placed in a furnace at 900°C for 15 minutes to foam. The cellulated bar was removed, placed in another furnace and slow cooled to room temperature. The foamed body was of the same configuration as the green body and had dimensions of 11/16″ × 3/4″ × 5 5/8″. This body had a uniform cellular structure and a density of 0.30 grams/cc.

Several bodies were prepared as in Example 1, but without grog, and fired at the temperatures shown. The bodies all foamed and yielded the densities shown below.

Example	Firing Temperature °C.	Density grams/cc
2	800	0.60
3	850	0.40
4	875	0.30
5	900	0.26
6	925	0.25
7	950	0.22

Example 8

A batch was prepared wherein the flux addition was completely sodium hydroxide, so that the total sodium hydroxide addition to the batch of Example 1 was 14 pounds. The batch was treated and the body was fired as in Example 1. The resultant product was a uniformly cellulated body having a density of 0.30 grams/cc.

Other bodies having the batch composition of Example 8, but without grog, were fired at the temperatures of Examples 2 to 7 inclusive. The resultant densities were essentially identical.

Example 9

A batch was prepared in a manner similar to that of Example 1, except that batch ingredients were as follows:

70.7 pounds Gonzales bentonite,
8 pounds sodium carbonate,
1 pound sodium acetate.

Those ingredients were ballmilled for two hours and then 39.6 pounds of a 15% Na_2O/30% SiO_2 sodium silicate solution was uniformly dispersed in the milled batch. The batch was then pressed and fired as in

Example 1. The resultant body was a uniformly cellulated body having a density of 0.30 grams/cc.

Other bodies having the batch composition of Example 8, but without grog. were fired at the temperatures of Examples 2 to 7 inclusive. The resultant densities were essentially identical.

Example 10

A batch was prepared as in Example 1, except that the amount of sodium carbonate was reduced to 4.25 pounds. This reduced the total flux from 12.8% to 10.4%. This reduction in flux increased the Al_2O_3 to 17%. This new batch was prepared, pressed and fired at 900°C as in Example 1, but without grog. The resultant body was uniformly cellulated and had a density of 0.45 grams/cc.

Three additional bodies were prepared as in Example 10 and were fired at the the temperatures shown below with the resultant densities as shown:

Example	Firing Temperature °C.	Density grams/cc
11	875	0.65
12	925	0.35
13	950	0.30

Example 14

A batch was prepared as in Example 1, except that the total flux was increased by increasing the amount of sodium carbonate to 12.6 pounds and the sodium hydroxide to 9.15 pounds. This increased the total alkali metal oxide flux to 19% and reduced the Al_2O_3 to 13%. The batch was then mixed, pressed and fired at 900°C. This firing produced a body having a density of 0.25 grams/cc.

Three additional bodies were prepared as in Example 14, fired at the temperatures shown below and produced the densities shown below:

Example	Firing Temperature °C.	Density grams/cc
15	800	0.45
16	850	0.35
17	870	0.30

Example 18

A batch was prepared as in Example 1, without grog and with the acetate being increased to 2%. The batch was then pressed and fired at 900°C. The resultant body had a density of 0.23 grams/cc.

Several other bodies having the same composition as Example 18 were fired at different temperatures as shown below:

Example	Firing Temperature °C.	Density grams/cc
19	875	0.23
20	925	0.25

Several samples were prepared as in Example 1, except that carbon black (as available from the Cabot Corp.) was substituted for sodium acetate, as the foaming agent. The following table shows the effect on density of increasing amounts of carbon black.

Example	Per cent Carbon Black	Density grams/cc
21	0.1	0.45
22	0.2	0.30
23	0.3	0.25
24	0.4	0.23
25	0.6	0.22
26	1.0	0.22

In the following group of examples, other organics were substituted for the sodium acetate of Example 1. otherwise all conditions were the same.

Example	Compound	Pounds	Density grams/cc
27	sodium oleate	0.4	0.34
28	sodium succinate	2,0	0.30
29	malonic acid	0.8	0.35

Example 30

A volcanic ash of approximately the following composition: 73% SiO_2, 14.3% Al_2O_3, 3% Na_2O, 4% K_2O, 1% Fe_2O_3 1% MgO, 0.5% CaO, having a moisture content of 0.5%, a loss on ignition of 3% and a grain size of 3 microns was milled for 4 hours with anhydrous NaOH and anhydrous sodium acetate. The milled batch consisted of 87 pounds volcanic ash, 11.8 pounds NaOH, and 1.2 pounds sodium acetate. This mixture was pressed into a bar and fired for 15 minutes at 900°C. The resultant body was cellulated and had a density of 0.30 grams/cc.

WHAT WE CLAIM IS:

1. A batch for making a cellulated glass body comprising, in weight percent on the anhydrous basis. at least 50% by weight of at least one rock which is volcanic ash, weathered volcanic ash, and/or clay, at least one alkali metal containing material in which sodium hydroxide and/or sodium silicate constitutes at least 25% by weight of the total content of such alkali metal containing material, and a cellulating agent which is carbon and/or a compound which thermally decomposes below the cellulating temperature and has carbon as a decomposition product, the total rock, alkali metal containing material, and cellulating agent being at least 75% by weight of the anhydrous batch and the batch comprising, in weight percent as calculated from the batch on the oxide basis, 10% to 20% total alkali metal oxide. SiO_2 and Al_2O_3 in the ratio of from 3:1 to 6:1, and a total content of alkali metal oxide, SiO_2 and Al_2O_3 that is at least 93%.

2. A batch as claimed in claim 1 wherein the rock is a clay containing a substantial quantity of illite or smectite mineral.

3. A batch as claimed in claim 2

wherein the clay contains montmorillonite as the smectite material.

4. A batch as claimed in claim 1 wherein the rock is a bentonite clay.

5   5. A batch as claimed in any of claims 1 to 4 wherein the average grain size of the weathered volcanic ash or clay is below 5 microns.

6. A batch as claimed in any of claims 10 1 to 5 wherein up to 20% by weight of the total alkali metal oxide is Li_2O and/or K_2O.

7. A batch as claimed in any of claims 1 to 6 wherein the carbon provided by the cellulating agent comprisese 0.1 to 1.0% 15 by weight of the anhydrous batch.

8. A batch as claimed in any of claims 1 to 7 wherein grog (as herein defined) comprises up to 25% by weight of the anhydrous batch.

20   9. A batch as claimed in claim 1 wherein bentonite clay comprises 70% to 87% by weight of the anhydrous batch, the alkali metal oxide containing materials are sodium hydroxide and sodium carbonate in equal 25 parts by weight and comprise 12% to 18% by weight of the anhydrous batch, and the cellulating agent is sodium acetate which comprisese 0.75 to 1.25% by weight of the anhydrous batch.

30   10. A batch as claimed in claim 1 substantially as herein described with reference to the Examples.

11. A cellulated glass body when prepared from a batch as claimed in any of claims 1 to 10.   35

12. A method for producing a cellulated glass body comprising the steps of mixing a batch as claimed in any of claims 1 to 10, shaping said batch to form an article of the desired configuration, and firing the 40 shaped body at a temperature above 800°C for a length of time sufficient to produce a body having a density between 0.15 and 0.65 grams/cc.

13. A method as claimed in claim 12 45 wherein the firing temperature is above 800°C but not above 950°C.

14. A method as claimed in claim 13 wherein the firing time is between 2 and 15 minutes.   50

15. A method as claimed in claim 12 substantially as herein described with reference to the Examples.

16. A cellulated glass body when prepared by a method as claimed in any of 55 claims 12 to 15.